

Dielectric relaxation of benzonitrile and tetramethyl urea with N, methylformamide in C₆H₆ under 9.885 GHz electric field

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Dielectric relaxation of binary (*jk*) polar mixtures of benzonitrile and tetramethyl urea (TMU) with N,methylformamide (NMF) dissolved in benzene (*i*) for different weight fractions w_{jk} 's of polar solutes and mole fraction x_j 's of NMF at 25, 30, 35 and 40 °C have been studied in terms of relaxation time τ_{jk} and dipole moment μ_{jk} from conductivity measurement of solution under 9.885 GHz electric field using Debye Model. Solute-solvent and solute-solute association have been predicted from plot of τ_{jk} and μ_{jk} against x_j 's of NMF up to $x_j=0.5$ and beyond $x_j=0.5$ to $x_j=1.0$, respectively. Estimated τ and μ from both the proposed methods agree with the reported values. Theoretically μ 's have been calculated from bond angles and bond moments of polar groups due to existence of inductive, mesmeric and electromeric effect arising out of microscopic inhomogeneity in them. Molecular dynamics of polar mixtures have been ascertained from Eyring rate equation to establish Debye relaxation mechanism for all systems.

Keywords: Dielectric relaxation, Dipole moment, Binary mixture, Dimer

1 Introduction

Dielectric investigations in polar liquids dissolved in non polar solvents provide meaningful information on structural and associational aspect as well as formation of molecular complexes in GHz electric field under varying conditions of complexation, temperature and environmental factors. It is of considerable interest to researchers because of the capacity of microwaves to detect weak molecular association¹⁻⁴. On the basis of the results, appropriate models^{5,6} of liquid mixture involving relaxation process have been formulated. Benzonitrile is a non aqueous excellent solvent for many anhydrous

Recently, Kumar *et al.*^{12,13} measured the dielectric relaxation parameters like real ϵ_{ijk}' and imaginary ϵ_{ijk}'' parts of complex relative permittivity ϵ_{ijk}^* of binary (*jk*) or single *j* or *k* polar molecule of (NMF+benzonitrile) and (NMF+TMU) dissolved in nonpolar solvent (*i*) benzene for different weight fractions w_{jk} 's, w_j 's or w_k 's at 25, 30 and 25, 30, 35 and 40 °C temperatures, respectively, for 0.0, 0.3, 0.5, 0.7 and 1.0 mole fractions x_j 's of NMF using standard standing wave microwave techniques and Gopala Krishna's single frequency (9.885 GHz) concentration variational method¹⁴. They intended to predict the solute-solvent (monomer) types of ternary mixture. The thermodynamic energy parameters for the dielectric relaxation and viscous flow process of the binary polar mixture were measured at different mole fraction of NMF to arrive at molecular environment.

We, therefore, thought to make an extensive study further with the available data on the binary (*jk*) polar mixture of (NMF+benzonitrile) and (NMF+TMU) dissolved in C₆H₆ in terms of measured real σ_{ijk}' and imaginary σ_{ijk}'' parts of high frequency complex conductivity σ_{ijk}^* for different weight fractions w_{jk} 's of polar solutes at 9.885 GHz electric field under the identical state of molecular environment^{12,13} in SI unit.

variety of organic substances. N-methylformamide (NMF) is an important non aqueous amide⁸ and a specialized solvent in oil refineries. The molecule contains a peptide linkage and a study of its hydrogen bonding yields insight into the nature of protein structures⁹. NMF is also a precursor in specialized amidation reactions and of considerable medical interest since it possesses anti tumour activities¹⁰. TMU is a useful non aqueous solvent for studying the behaviour of electrolytes in solution¹¹.

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The conductivity measurement technique is concerned with bound molecular charge of the polar molecules unlike permittivity ϵ_{ijk} 's and susceptibility χ_{ijk} 's which are related to all types of polarization and orientational polarization, respectively. In recent past, conductivity measurement technique¹⁵ in the microwave electric fields has been successfully applied on binary polar mixture¹⁶ as well as single polar liquid molecules⁵ dissolved in nonpolar solvents. However, no such rigorous study has been made so far on the associative binary polar mixtures of (NMF+Benzonitrile) and (NMF+TMU) dissolved in C_6H_6 at a temperature under 9.885 GHz electric field using conductivity measurement technique. Dielectric measurement also has uses in package design, process control and physical chemical analysis¹⁷. The purpose of the conductivity measurement technique concerning bound molecular charge of the polar molecule allows one to link the results of dielectric studies to throw light on structure and dynamics of polar liquid mixture in solution inferred from other techniques¹⁴. Under a definite temperature, dielectric relaxation phenomena should be closely related to variational frequency. After all only the conductivity under 9.885 GHz is measured. Even though 9.885 GHz is the characteristics frequency of this dielectric relaxation but for different system or the same system with the different concentrations, the characteristic frequency of the dielectric relaxation may also be changed. The aim of the present paper is also to see the applicability of conductivity measurement technique within the frame work of Debye model in ternary liquid mixture under high frequency (9.885 GHz) electric field like earlier¹⁶.

2 Experimental Details

The solvents NMF (Fluka, Germany), benzonitrile (Merck, Germany) and TMU (Fluka, Germany) are all good quality pure samples. NMF was dried with 4Å molecular sieves for about 10 h and then distilled through a long vertical fractionating column under reduced pressure^{12,13}. TMU was dried over anhydrous Bao for 48 h and then distilled through a long vertical fractionating columnlike benzonitrile. Both of above three cases, the middle fraction of the sample was collected and the mixed together for preparation of the binary polar mixture of weight fractions w_{jk} 's dissolved in benzene. The X band microwave was used to measure ϵ_{ijk}' , ϵ_{ij}' and ϵ_{ik}' and ϵ_{ijk}'' , ϵ_{ij}'' and ϵ_{ik}'' at 25, 30, 35 and 40 °C temperatures and

different w_{jk} 's, respectively^{12,13}. The temperature of the dielectric cell was maintained within the accuracy limit of ± 0.05 °C through circulating water and a thermostat. The measured ϵ_{ijk}' and ϵ_{ijk}'' are accurate within $\pm 0.5\%$ and $\pm 3.8\%$, respectively. The measured data are simply normalized to get σ_{ijk}' and σ_{ijk}'' within accuracy limit.

3 Theoretical Formulations

The σ_{ijk}^* due to displacement current of a binary polar liquid mixture dissolved in non polar solvent (*i*) for a given w_{jk} 's of solute is¹⁸:

$$\sigma_{ijk}^* = \sigma_{ijk}' + j\sigma_{ijk}'' \quad \dots (1)$$

Where $\sigma_{ijk}' = \omega \epsilon_0 \epsilon_{ijk}''$ and $\sigma_{ijk}'' = \omega \epsilon_0 \epsilon_{ijk}'$ are the real and imaginary parts of complex conductivity σ_{ijk}^* at different weight fractions w_{jk} 's of polar mixture. ϵ_0 is the absolute permittivity of free space = 8.854×10^{-12} F.m⁻¹. The $\sigma_{ijk}'-w_{jk}$ and $\sigma_{ijk}''-w_{jk}$ curves are plotted in Figs 1 and 2.

The total conductivity σ_{ijk} of the ternary solution is:

$$\sigma_{ijk} = \omega \epsilon_0 \sqrt{(\epsilon_{ijk}''^2 + \epsilon_{ijk}'^2)} = \sqrt{(\sigma_{ijk}'^2 + \sigma_{ijk}''^2)} \quad \dots (2)$$

The imaginary parts of conductivity σ_{ijk}'' is related to σ_{ijk}' by the following relation:

$$\sigma_{ijk}'' = \sigma_{\infty ij k} + (1/\omega\tau_{jk}) \sigma_{ijk}' \quad \dots (3)$$

or, $\tau_{jk} = 1/\omega\beta'$

where β' is the slope of $\sigma_{ijk}''- \sigma_{ijk}'$ linear relation as shown Fig. 3 and given in Table 1.

The constituent polar molecules mixed in appropriate proportions yields average τ_{mix} as:

$$\tau_{mix} = \tau_j x_j + \tau_k x_k \quad \dots (4)$$

Where x_j and x_k are the mole fraction of *j*(NMF) and *k*(TMU or benzonitrile), respectively.

Both σ_{ijk}'' and σ_{ijk}' are the functions of w_{jk} 's at different temperatures. To eliminate the effect of polar-polar interactions in the estimation of τ_{jk} , one can safely use Eq. (3) in following form:

$$\tau = \frac{1}{\omega} \frac{\beta_2}{\beta_1} \quad \dots (5)$$

Where β_2 and β_1 are the slopes of $\sigma_{ijk}''- w_{jk}$ and $\sigma_{ijk}'- w_{jk}$ curves at $w_{jk} \rightarrow 0$ of Figs 1 and 2, respectively as given in Table 1. τ 's are estimated from both the methods of Eqs (3) and (5) and they are given in

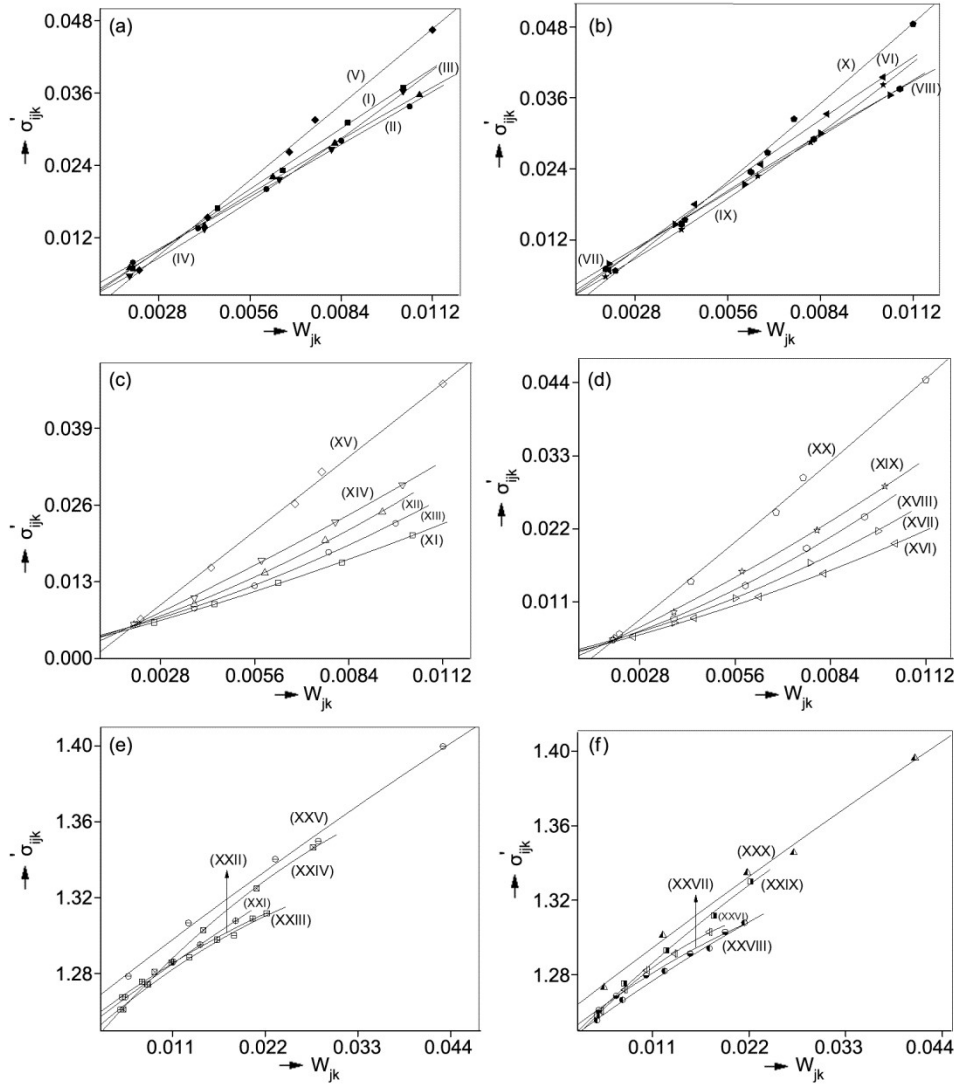


Fig. 1 — The variation of real part of conductivity σ'_{ijk} ($\text{ohm}^{-1}\text{m}^{-1}$) against weight fractions w_{jk} 's of binary polar mixture dissolved in C_6H_6 under 9.885 GHz electric field; (a) NMF+benzonitrile (I) ■ (II) • (III) ▲ (IV) ▼ (V) ◆ at 25 °C; (b) NMF+benzonitrile (VI) ◀ (VII) ▶ (VIII) ● (IX) ★ (X) ◆ at 30 °C for 0.0,0.3,0.5,0.7 and 1.0 x_j of NMF, respectively; (c) NMF+TMU (XI) □ (XII) ○ (XIII) △ (XIV) ▽ (XV) ◇ at 25 °C; (d) NMF+TMU (XVI) ◁ (XVII) ▷ (XVIII) ○ (XIX) ☆ (XX) △ at 30 °C; (e) NMF+TMU (XXI) ⊕ (XXII) ⊞ (XXIII) ⊚ (XXIV) ⊛ (XXV) ⊙ at 35 °C; (f) NMF+TMU (XXVI) † (XXVII) ‡ (XXVIII) • (XXIX) ▣ (XXX) ▲ at 40 °C for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively.

Table 1 for different x_j 's of NMF along with reported τ 's due to Gopalakrishna method¹⁴.

In the high frequency region, $\sigma'_{ijk} \approx \sigma_{ijk}$, Eq. (3) can now be written as:

$$\beta = \frac{1}{\omega\tau_{jk}} \left(\frac{d\sigma'_{ijk}}{dw_{jk}} \right)_{w_{jk} \rightarrow 0} \dots (6)$$

where β is the slope of σ_{ijk} - w_{jk} curves of Fig. 4 at $w_{jk} \rightarrow 0$ and given in Table 2. The estimated τ_{jk} and μ_{jk} of Table 1 and Table 2 are plotted against x_j of the NMF as seen in Fig. 5.

At $w_{jk} \rightarrow 0$, the real part σ'_{ijk} of a binary polar-non polar liquid mixture of w_{jk} at T K is given by^{13,18}:

$$\left(\frac{d\sigma'_{ijk}}{dw_{jk}} \right)_{w_{jk} \rightarrow 0} = \frac{N\rho_i\mu_{jk}^2}{3M_{jk}K_B T} \frac{\omega^2\tau_{jk}}{(1+\omega^2\tau_{jk}^2)} \frac{(\epsilon_i+2)^2}{3^2} \dots (7)$$

where μ_{jk} is the dipole moment of binary polar mixture of molecular weight $M_{jk}=M_jx_j+M_kx_k$; x_j being the mole fractions of NMF in the binary polar mixture of j (NMF) and k (benzonitrile or TMU) such that $x_j+x_k=1$. The other terminologies and symbols are of usual significance⁵. On comparison of Eqs (6) and (7) one gets:

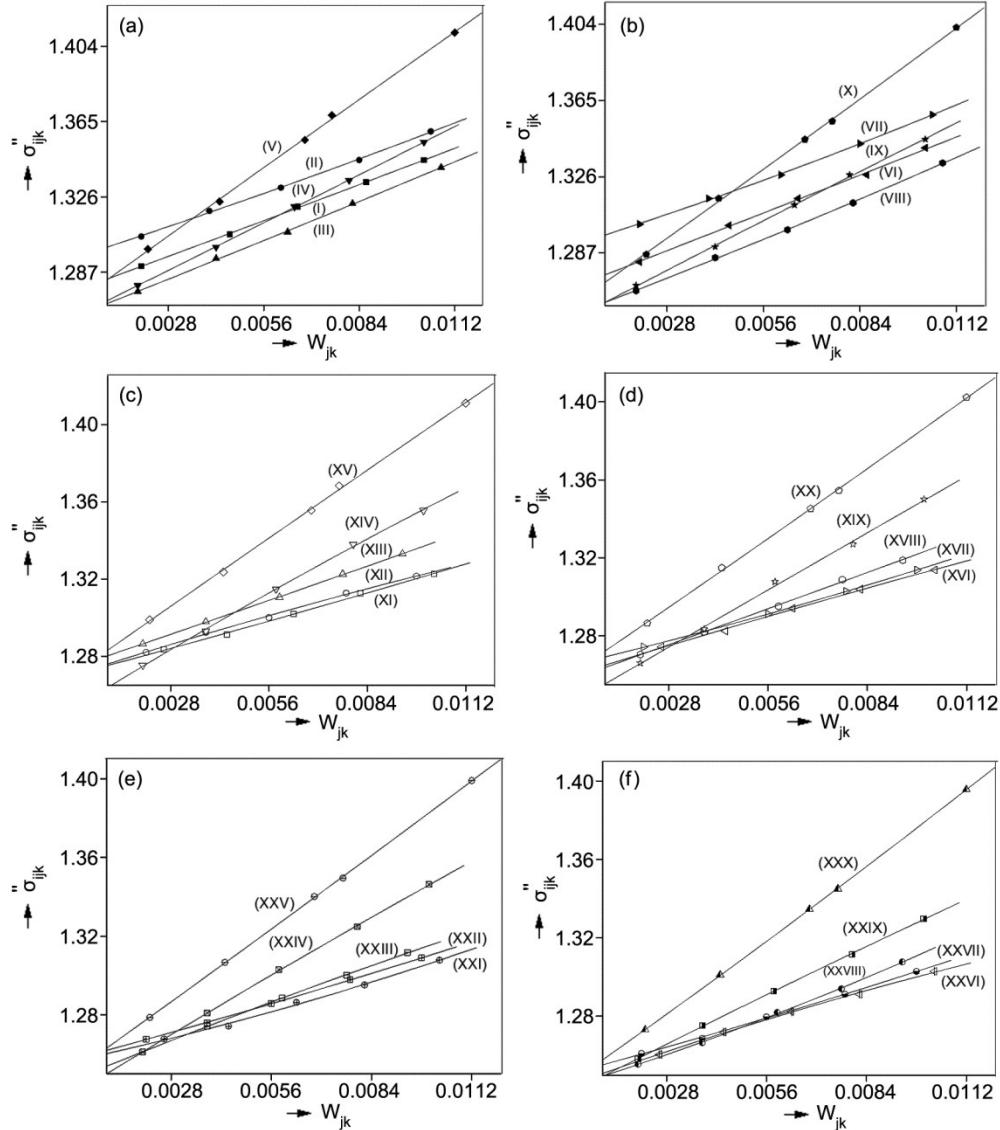


Fig. 2 — The variation of imaginary part of conductivity σ''_{ijk} ($\text{ohm}^{-1}\text{m}^{-1}$) against weight fractions w_{jk} 's of binary polar mixture dissolved in C_6H_6 under 9.885 GHz electric field; (a) NMF+benzonitrile (I) \blacksquare (II) \bullet (III) \blacktriangle (IV) \blacktriangledown (V) \blacklozenge at 25 °C; (b) NMF+benzonitrile (VI) \blacktriangleleft (VII) \blacktriangleright (VIII) \bullet (IX) \star (X) \blacklozenge at 30 °C for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively; (c) NMF+TMU (XI) \square (XII) \circ (XIII) \triangle (XIV) \triangledown (XV) \diamond at 25 °C; (d) NMF+TMU (XVI) \triangleleft (XVII) \triangleright (XVIII) \circ (XIX) \star (XX) \triangle at 30 °C; (e) NMF+TMU (XXI) \oplus (XXII) \boxplus (XXIII) \boxminus (XXIV) \boxtimes (XXV) \ominus at 35 °C; (f) NMF+TMU (XXVI) \blacklozenge (XXVII) \bullet (XXVIII) \blacklozenge (XXIX) \blacksquare (XXX) \blacktriangle at 40 °C for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively.

$$\mu_{jk} = \left[\frac{27M_{jk}K_B T \beta}{N \rho_i (\epsilon_i + 2)^2 \omega b} \right]^{1/2} \quad \dots (8)$$

where $b=1/(1+\omega^2\tau_{jk}^2)$ is the dimensionless parameter. The other symbols used in Eq. (8) carry usual meanings⁵ in SI unit. All the μ 's at different x_j 's of TMF along with μ_{theo} 's are given in Table 2.

4 Result and Discussion

The normalised conductivity data σ_{ijk} 's of the binary (jk) polar mixtures of N, methyl formamide

(NMF) + benzonitrile and NMF+ tetra-methyl urea (TMU) dissolved in C_6H_6 for 0.0, 0.3, 0.5, 0.7, and 1.0 mole fraction x_j 's of NMF at 25, 30, 35 and 40 °C, respectively, under 9.885 GHz electric field were estimated at different weight functions w_{jk} 's of solute. They are used to estimate τ_{jk} of binary polar mixture using ratio of slopes of $\sigma_{ijk}''-w_{jk}$ and $\sigma_{ijk}'-w_{jk}$ curve as well as $\sigma_{ijk}''-\sigma_{ijk}'$ linear slope as shown in Table 1. It is evident from Table 1 that τ 's from ratio of slopes higher in magnitude than linear slope for all systems

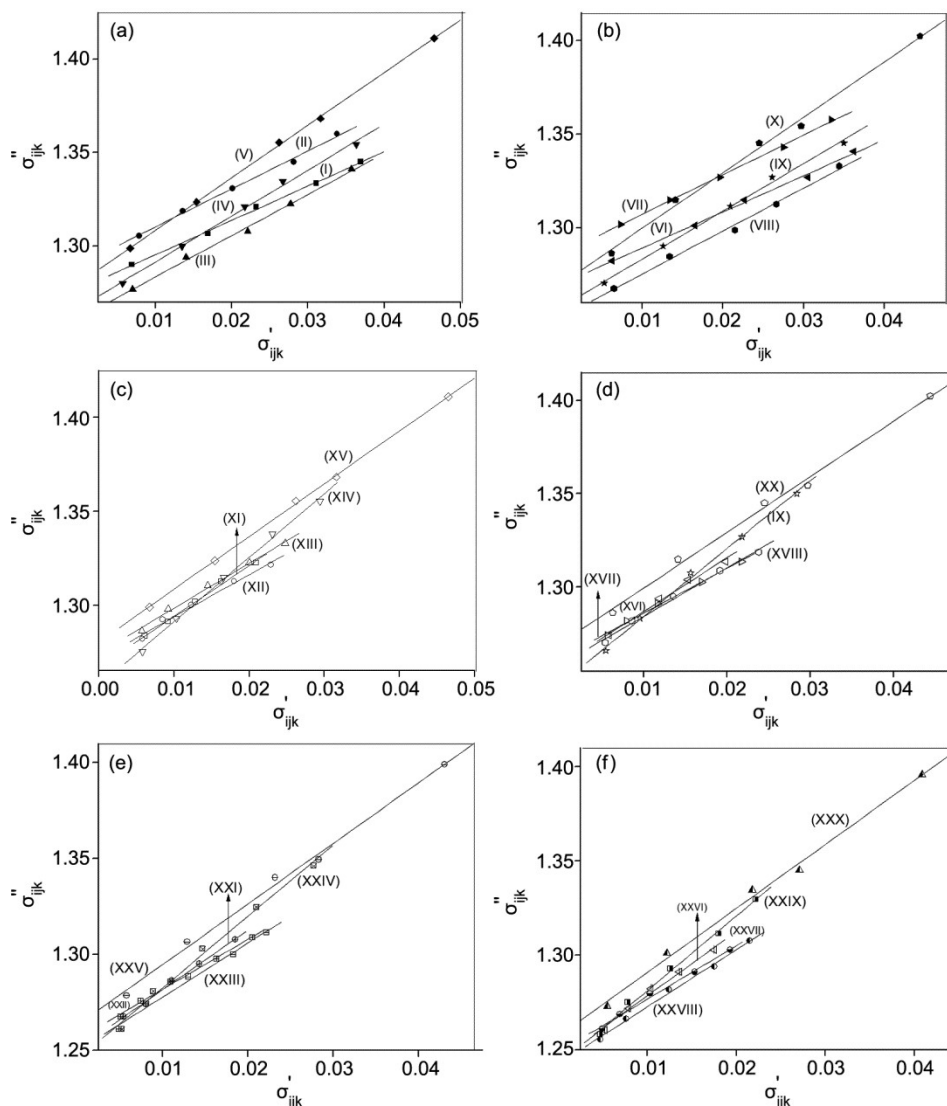


Fig. 3 — Linear variation of imaginary part of conductivity σ''_{ijk} against real part of conductivity σ'_{ijk} of binary polar mixture dissolved in C_6H_6 under 9.885 GHz electric field; (a) NMF+benzonitrile (I) ■ (II) ● (III) ▲ (IV) ▼ (V) ◆ 25 °C; (b) NMF+benzonitrile (VI) ◀ (VII) ▶ (VIII) ● (IX) ★ (X) ◆ at 30 °C for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively; (c) NMF+TMU (XI) □ (XII) ○ (XIII) △ (XIV) ▽ (XV) ◇ at 25 °C; (d) NMF+TMU (XVI) ◁ (XVII) ▷ (XVIII) ○ (XIX) ☆ (XX) △ at 30 °C; (e) NMF+TMU (XXI) ⊕ (XXII) ⊞ (XXIII) ⊟ (XXIV) ⊠ (XXV) ⊖ at 35 °C; (f) NMF+TMU (XXVI) ♠ (XXVII) ♡ (XXVIII) ♢ (XXIX) ▣ (XXX) ▲ at 40 °C for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively.

except NMF+benzonitrile at 0.7, 1.0 and 0.0, 0.3, 0.5 and 1.0 x_j 's of NMF for NMF+TMU polar mixtures at 25 °C and 30 °C, respectively. Comparatively larger magnitude of τ_{ijk} for (NMF+TMU) at 35 °C and 40 °C for x_j 's 0.0, 0.3 and 0.0, 0.3, 0.5, respectively, are also noted. This type of the behaviors due to existence of solvent effect¹⁸ at infinite dilution (i.e. $w_{jk} \rightarrow 0$) as polar-polar interaction is almost avoided in the ratio of slopes method compared to linear slope to yield low τ 's. Significant existence of solute-solute interaction at infinite dilution may occur for

associating liquid mixture of NMF, benzonitrile and TMU in C_6H_6 at a certain concentration and extrapolation at infinite dilution then become uncertain leading to larger τ and μ . Although, τ 's from both the methods including τ_{mix} using ratio of slope agree well with the reported values (Gopalakrishna method). All the τ 's are placed in Table 1 obeying Debye relaxation mechanism except at 35 °C and 40 °C of (NMF+TMU) mixture for 0.0, 0.3 and 0.0, 0.3, 0.5, 0.7 x_j 's of NMF from ratio of slopes method. Effective viscosity of solvent and appreciable sticking

Table 1 — Measured relaxation times τ 's using $\sigma_{ijk}'' - \sigma_{ijk}'$ linear curve Eq. (3) as well as the ratio of slopes of $\sigma_{ijk}'' - w_{jk}$ and $\sigma_{ijk}' - w_{jk}$ curves at $w_{jk} \rightarrow 0$ of Eq. (5), reported τ 's due to Gopalakrishna method, average τ_{mix} of binary polar mixture NMF + benzonitrile and NMF + TMU binary polar mixture dissolved in C_6H_6 for 0.0, 0.3, 0.5, 0.7 and 1.0 mole fraction of NMF at 25 °C, 30 °C and 25 °C, 30 °C, 35 °C, 40 °C, respectively, under 9.885 GHz electric field.

System	Temperature (°C)	Mole fraction x_j of NMF	Ratio of slopes of $\sigma_{ijk}'' - w_{jk}$ and $\sigma_{ijk}' - w_{jk}$ curves at $w_{jk} \rightarrow 0$ of Eq. (5)	Slope of $\sigma_{ijk}'' - \sigma_{ijk}'$ curves of Eq. (3)	τ from ratio of slope (ps)	τ from linear slope (ps)	Calculated average $\tau_{mix} = \tau_j x_j + \tau_k x_k$ from Eq. (4) (ps)	Reported τ (GK) (ps)
(I) NMF+Benzonitrile in C_6H_6	25	0.0	1.7640	1.8397	9.13	8.66	9.13	8.38
(II) NMF+Benzonitrile in C_6H_6	25	0.3	1.8762	2.03361	8.58	7.84	8.07	7.52
(III) NMF+Benzonitrile in C_6H_6	25	0.5	1.9534	2.20541	8.24	7.23	7.37	6.89
(IV) NMF+Benzonitrile in C_6H_6	25	0.7	3.0106	2.45336	5.35	6.50	6.66	6.23
(V) NMF+Benzonitrile in C_6H_6	25	1.0	2.8759	2.81128	5.60	5.67	5.60	5.35
(VI) NMF+Benzonitrile in C_6H_6	30	0.0	1.7962	1.92351	8.96	8.29	8.96	7.96
(VII) NMF+Benzonitrile in C_6H_6	30	0.3	1.8131	2.11186	8.88	7.55	7.82	7.27
(VIII) NMF+Benzonitrile in C_6H_6	30	0.5	1.8651	2.2965	8.63	6.94	7.06	6.64
(IX) NMF+Benzonitrile in C_6H_6	30	0.7	3.1999	2.55057	5.03	6.25	6.29	5.60
(X) NMF+Benzonitrile in C_6H_6	30	1.0	3.1255	2.96642	5.15	5.37	5.15	5.05
(XI) NMF+TMU in C_6H_6	25	0.0	3.3524	2.70582	4.80	5.95	4.80	5.72
(XII) NMF+TMU in C_6H_6	25	0.3	4.4078	2.2421	3.65	7.18	5.04	6.84
(XIII) NMF+TMU in C_6H_6	25	0.5	3.8063	2.39904	4.23	6.71	5.20	6.43
(XIV) NMF+TMU in C_6H_6	25	0.7	4.4323	3.41573	6.63	4.71	5.36	4.42
(XV) NMF+TMU in C_6H_6	25	1.0	2.8759	2.82128	5.60	5.72	5.60	5.35
(XVI) NMF+TMU in C_6H_6	30	0.0	4.8396	2.87152	3.29	5.61	3.29	5.35
(XVII) NMF+TMU in C_6H_6	30	0.3	3.9140	2.402	4.11	6.70	3.85	6.43
(XVIII) NMF+TMU in C_6H_6	30	0.5	4.7988	2.58306	3.36	6.23	4.22	5.96
(XIX) NMF+TMU in C_6H_6	30	0.7	4.8652	3.61976	3.31	4.45	4.59	4.24
(XX) NMF+TMU in C_6H_6	30	1.0	3.1255	2.96642	5.15	5.43	5.15	5.05
(XXI) NMF+TMU in C_6H_6	35	0.0	1.1429	3.10784	14.09	5.18	14.09	4.98
(XXII) NMF+TMU in C_6H_6	35	0.3	1.4178	2.60417	11.36	6.18	11.17	5.93
(XXIII) NMF+TMU in C_6H_6	35	0.5	1.8701	2.81357	8.61	5.72	9.22	5.42
(XXIV) NMF+TMU in C_6H_6	35	0.7	2.1612	3.72114	7.45	4.33	7.27	4.05
(XXV) NMF+TMU in C_6H_6	35	1.0	3.7016	3.15981	4.35	5.10	4.35	4.72
(XXVI) NMF+TMU in C_6H_6	40	0.0	1.2106	3.40286	13.30	4.73	13.30	4.57
(XXVII) NMF+TMU in C_6H_6	40	0.3	1.2836	2.8213	12.54	5.71	10.70	5.49
(XXVIII) NMF+TMU in C_6H_6	40	0.5	1.5881	3.01732	10.14	5.34	8.96	5.10
(XXIX) NMF+TMU in C_6H_6	40	0.7	2.0070	3.94194	8.02	4.08	7.22	3.87
(XXX) NMF+TMU in C_6H_6	40	1.0	3.4879	3.3849	4.62	4.76	4.62	4.41

of molecules due to inter molecular interaction energy exceeding $K_B T$ at higher temperature may be the cause for such deviation. The variation of σ_{ijk}' against w_{jk} 's are shown in Fig. 1, it is evident that all the nonlinear curves of (NMF+ benzonitrile) in C_6H_6 at 25 °C and 30 °C, respectively, are overlapping with greater magnitude of x_j 's = 1.0 of NMF. It is also observed that the plot of σ_{ijk}' against w_{jk} of (NMF+TMU) in C_6H_6 gradually rises from 0.0 to 1.0 x_j 's of NMF at all the temperatures. This is due to rise in absorption of hf electric energy when x_j 's of NMF increases. The variation of σ_{ijk}'' against w_{jk} is also parabolic as seen in Fig. 2. For all the systems of (NMF+benzonitrile) in C_6H_6 show σ_{ijk}'' maximum for $x_j = 1.0$ and minimum for $x_j = 0.5$ of NMF, whereas σ_{ijk}'' 's gradually rise to maximum from $x_j = 0.0$ to $x_j = 1.0$ for (NMF+TMU) in C_6H_6 at all temperatures. This is due to the fact that polarization of binary polar mixture increase from $x_j = 0.0$ to 1.0 with the

absorption of hf electric energy as evident from $\sigma_{ijk}' - w_{jk}$ curve. The variation of $\sigma_{ijk}'' - \sigma_{ijk}'$ linear equations is sketched in Fig. 3. Greater τ 's are observed for benzonitrile ($x_j = 0$) and the value gradually decreases from $x_j = 0.0$ to 1.0 of NMF to exhibit low value at 25 °C and 30 °C. In case of (NMF+TMU) in C_6H_6 all the τ 's increase from $x_j = 0$ to 0.3 of NMF to show maximum and then decrease gradually to exhibit minimum value at $x_j = 1.0$ of NMF. The graphs are overcrowded for (NMF+TMU) in C_6H_6 except for pure NMF, showing higher value of hf electric energy absorption in all the systems. The slopes and intercepts of the curves are very close probably due to more or less same dipole moment of the two constituent binary polar mixture¹⁹. Similar observation is noted for τ from ratio of slopes for all the systems except (NMF+TMU) in C_6H_6 at 25 °C and 30 °C where maximum τ is observed for $x_j = 0.7$ and 1.0, respectively. The $\sigma_{ijk}'' - w_{jk}$ curve in Fig. 4 are

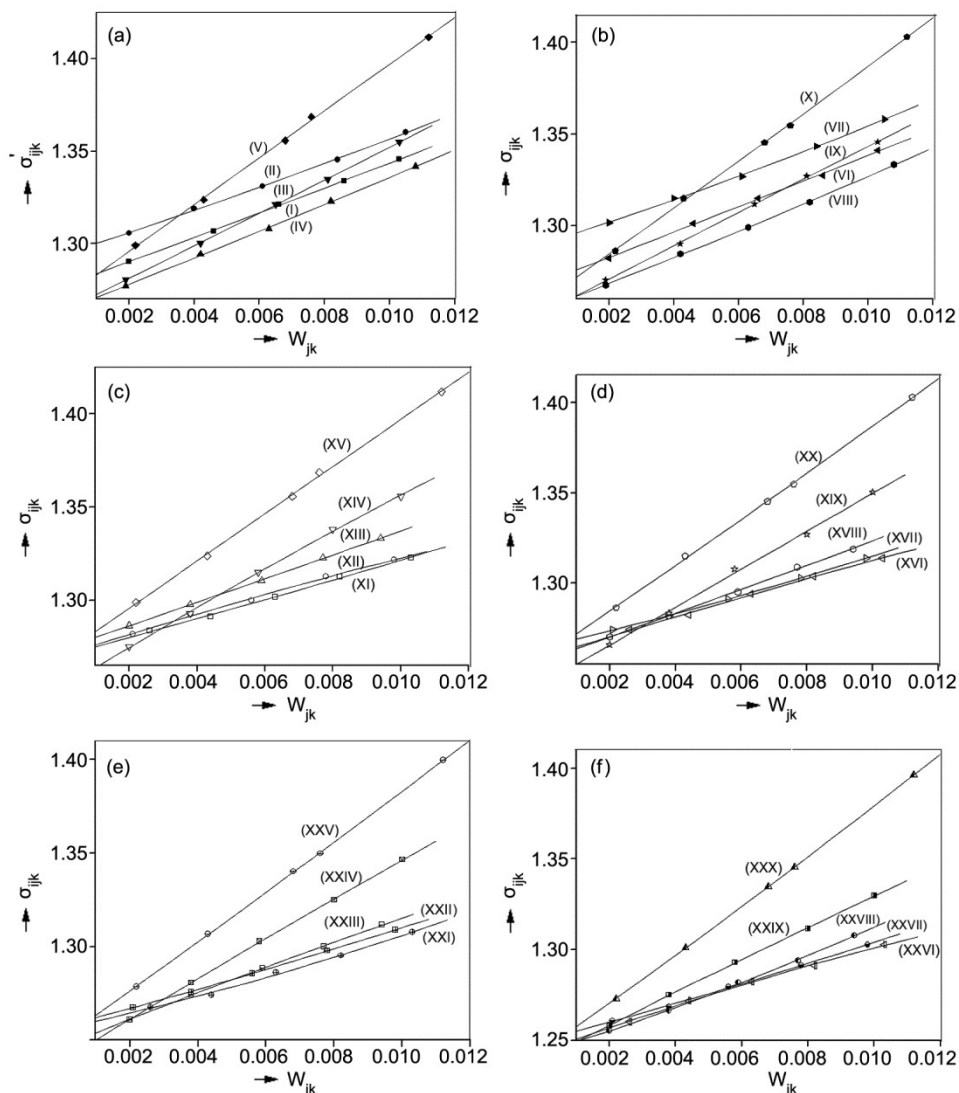


Fig. 4 — The variation of total conductivity σ_{ijk} ($\text{ohm}^{-1}\text{m}^{-1}$) against weight fractions w_{jk} 's of binary polar mixture dissolved in C_6H_6 under 9.885 GHz electric field; (a) NMF+benzonitrile (I) \blacksquare (II) \bullet (III) \blacktriangle (IV) \blacktriangledown (V) \blacklozenge at 25 °C; (b) NMF+benzonitrile (VI) \blacktriangleleft (VII) \blacktriangleright (VIII) \bullet (IX) \star (X) \blacklozenge at 30 °C for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively; (c) NMF+TMU (XI) \square (XII) \circ (XIII) \triangle (XIV) ∇ (XV) \diamond at 25 °C; (d) NMF+TMU (XVI) \triangleleft (XVII) \triangleright (XVIII) \circ (XIX) \star (XX) \diamond at 30 °C; (e) NMF+TMU (XXI) \oplus (XXII) \boxplus (XXIII) \boxtimes (XXIV) \boxtimes (XXV) \ominus at 35 °C; (f) NMF+TMU (XXVI) \blackspadesuit (XXVII) \ominus (XXVIII) \bullet (XXIX) \blacksquare (XXX) \blacktriangle at 40 °C for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively.

identical in nature of $\sigma_{ijk}''-w_{jk}$ curve of Fig. 2 signifying the validity of $\sigma_{ijk}'' \cong \sigma_{ijk}$. All the graphs of $\tau_{jk}-x_j$ and $\mu_{jk}-x_j$ as displayed in Fig. 5 are nonlinear. Unlike the system (NMF+TMU) in C_6H_6 at 25 °C and 30 °C all the curves show maximum τ_{jk} at $x_j = 0$ of NMF and then decreases gradually to show low τ 's at $x_j = 1.0$ of NMF. The trend of variation of τ_{jk} and μ_{jk} up to $x_j = 0.5$ of NMF is quite obvious as demanded by Eq. (8). The variations of μ_{jk} against x_j are found to decrease first showing minimum around $x_j = 0.5$ and increases thereafter to show maximum value. This is

explained on the basis of the fact solute- solvent molecular association happens up to $x_j = 0.5$, thereafter rupture of monomer occurs under hf electric field to facilitated solute-solute molecular association due to azeotropic behaviors arising from microscopic inhomogeneity of polar constituents²⁰. The $(\mu_{jk}-t)$ curve of Fig. 6 for (NMF+TMU) in C_6H_6 are usually nonlinear showing convex shape for highest asymmetric nature attained at $x_j = 0.5$ and 0.7 of NMF unlike others system of concave shape. The linear behavior is noted for (NMF+ benzonitrile) in C_6H_6 for

Table 2 — Slopes β 's of $\sigma_{ijk} - w_{jk}$ curve, dimensionless parameters b 's in terms of τ 's from Eqs (3) and (5), measured μ 's in two methods, average $\mu_{jk} = \mu_j x_j + \mu_k x_k$, reported μ 's as well as μ_{theo} 's in C.m of NMF + benzonitrile and NMF + TMU binary polar mixture dissolved in C_6H_6 for 0.0, 0.3, 0.5, 0.7 and 1.0 mole fraction of NMF at 25 °C, 30 °C and 25 °C, 30 °C, 35 °C, 40 °C, respectively, under 9.885 GHz electric field.

System	Temperature (°C)	Mole fraction x_j of NMF	Slope β 's of $\sigma_{ijk} - w_{jk}$ curve of Eq. (6)	$b = \frac{1}{1 + \omega^2 \tau^2}$ from τ of Eq. (5)	$b = \frac{1}{1 + \omega^2 \tau^2}$ from τ of Eq. (3)	μ from ratio of slope (C.m)	μ from linear slope (C.m)	Calculated average $\mu_{av} = \mu_j x_j + \mu_k x_k$ (C.m)	Reported μ (GK) (C.m)
(I) NMF+Benzonitrile in C_6H_6	25	0.0	6.53102	1.3216	1.2893	12.85	12.70	12.85	12.42
(II) NMF+Benzonitrile in C_6H_6	25	0.3	5.77637	1.2840	1.2371	11.13	10.92	10.98	-
(III) NMF+Benzonitrile in C_6H_6	25	0.5	7.0014	1.2619	1.2016	11.53	11.25	11.29	-
(IV) NMF+Benzonitrile in C_6H_6	25	0.7	8.68932	1.1104	1.1630	11.38	11.65	11.69	-
(V) NMF+Benzonitrile in C_6H_6	25	1.0	12.75215	1.1210	1.1240	12.52	12.54	12.52	11.92
(VI) NMF+Benzonitrile in C_6H_6	30	0.0	6.86569	1.3097	1.2651	13.30	13.07	13.30	12.73
(VII) NMF+Benzonitrile in C_6H_6	30	0.3	5.60493	1.3042	1.2199	11.19	10.83	10.90	-
(VIII) NMF+Benzonitrile in C_6H_6	30	0.5	6.73823	1.2873	1.1858	11.58	11.12	11.15	-
(IX) NMF+Benzonitrile in C_6H_6	30	0.7	9.21297	1.0976	1.1507	11.81	12.09	12.01	-
(X) NMF+Benzonitrile in C_6H_6	30	1.0	12.3679	1.1023	1.1112	12.39	12.44	12.39	12.12
(XI) NMF+TMU in C_6H_6	25	0.0	4.82990	1.0889	1.1366	10.65	10.88	10.65	11.19
(XII) NMF+TMU in C_6H_6	25	0.3	5.89541	1.0514	1.1989	10.67	11.40	10.91	-
(XIII) NMF+TMU in C_6H_6	25	0.5	6.16805	1.0690	1.1737	10.36	10.85	10.53	-
(XIV) NMF+TMU in C_6H_6	25	0.7	11.29246	1.1696	1.0856	12.96	13.17	13.32	-
(XV) NMF+TMU in C_6H_6	25	1.0	12.75215	1.1210	1.1262	12.52	12.55	12.52	12.12
(XVI) NMF+TMU in C_6H_6	30	0.0	5.70548	1.0418	1.1214	11.47	11.90	11.47	11.19
(XVII) NMF+TMU in C_6H_6	30	0.3	4.35166	1.0652	1.1732	9.35	9.82	9.32	-
(XVIII) NMF+TMU in C_6H_6	30	0.5	6.47713	1.0436	1.1497	10.63	11.15	10.75	-
(XIX) NMF+TMU in C_6H_6	30	0.7	10.55535	1.0423	1.0764	12.64	12.85	12.88	-
(XX) NMF+TMU in C_6H_6	30	1.0	12.3679	1.1023	1.1137	12.39	12.46	12.39	12.12
(XXI) NMF+TMU in C_6H_6	35	0.0	3.92161	1.7658	1.1035	12.55	9.92	12.55	11.26
(XXII) NMF+TMU in C_6H_6	35	0.3	4.80529	1.4978	1.1473	11.81	10.34	11.75	-
(XXIII) NMF+TMU in C_6H_6	35	0.5	7.47348	1.2860	1.1262	12.84	12.02	13.05	-
(XXIV) NMF+TMU in C_6H_6	35	0.7	11.27289	1.2141	1.0723	14.29	13.43	14.23	-
(XXV) NMF+TMU in C_6H_6	35	1.0	12.93531	1.0730	1.1003	12.67	12.83	12.67	12.49
(XXVI) NMF+TMU in C_6H_6	40	0.0	6.55233	1.6824	1.0863	16.04	12.89	16.04	11.49
(XXVII) NMF+TMU in C_6H_6	40	0.3	4.84677	1.6066	1.1258	12.45	10.42	11.79	-
(XXVIII) NMF+TMU in C_6H_6	40	0.5	5.71289	1.3966	1.1100	11.85	10.56	11.48	-
(XXIX) NMF+TMU in C_6H_6	40	0.7	9.31470	1.2481	1.0642	13.34	12.32	13.09	-
(XXX) NMF+TMU in C_6H_6	40	1.0	12.74525	1.0823	1.0874	12.79	12.82	12.79	12.73

all x_j 's at 25 °C and 30 °C, respectively. This type of behaviors is due to elongation of bond angles and bond moments with the rise of temperature under GHz electric field. Again the breaking of solute-solute or solute-solvent association with temperature may increases μ_{jk} values. The linear plot of $\ln(\tau_{jk}T)$ against $\frac{1}{T}$ curve from ratio of slopes method is sketched in

Fig. 7 using Eyring rate theory¹². The thermodynamic energy parameters like enthalpy of activation ΔH_e , free energy of activation ΔF_e , entropy of activation ΔS_e and ΔH_η due to viscous flow of the solvent were estimated and placed in Table 3. ΔH_e 's are -ive for all system except at 0.0, 0.7 and 1.0 x_j 's of NMF for (NMF+benzonitrile) and $x_j = 1.0$ of (NMF+TMU)

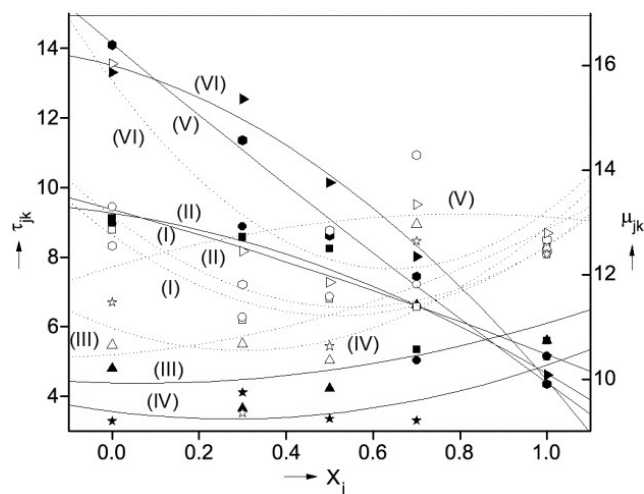


Fig. 5 — Variation of τ_{jk} 's in p sec as well as μ_{jk} 's (C.m) against x_j of NMF under 9.885 GHz electric field: (I) ■ and □ (II) • and ○ for binary polar mixture of NMF+benzotrile at 25 °C and 30 °C, respectively; (III) ▲ and △ (IV) ★ and ☆ (V) ● and ○ (VI) ► and ▷ for binary polar mixture of NMF+TMU at 25 °C, 30 °C, 35 °C and 40 °C, respectively.

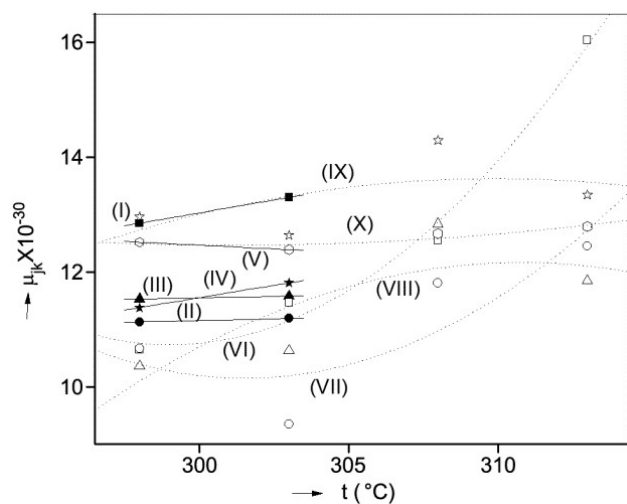


Fig. 6 — Plot of dipole moment μ_{jk} against temperature t in °C of binary polar mixture of NMF+benzotrile and NMF+TMU dissolved in C_6H_6 under 9.885 GHz electric field. (I) ■ (II) • (III) ▲ (IV) ★ (V) ● for NMF+benzotrile; (VI) □ (VII) ○ (VIII) △ (IX) ☆ (X) ○ for NMF+TMU for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively.

whereas ΔH_η is +ive. Enthalpy of activation depends upon the bonding nature of the molecules and excitation to the activated state involves breaking of bonds. Difference in ΔH_τ and ΔH_η indicates dielectric relaxation process involves different types of bonding and breaking of bonds to different extent. The value of $\gamma (= \frac{\Delta H_\tau}{\Delta H_\eta}) > 0.55$ for (NMF+ benzotrile) in C_6H_6 at $x_j = 0.7$ and 1.0 exhibiting the polar mixture do not behave as solid phase rotator whereas $\gamma < 0.45$ for rest

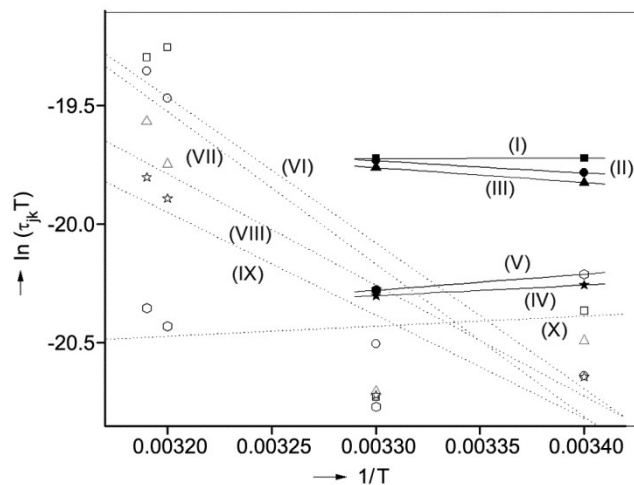


Fig. 7 — Linear plot of $\ln(\tau_{jk}T)$ against $1/T$ curve of binary polar mixture of NMF+benzotrile and NMF+TMU dissolved in C_6H_6 under 9.885 GHz electric field. (I) ■ (II) • (III) ▲ (IV) ★ (V) ● for NMF+benzotrile; (VI) □ (VII) ○ (VIII) △ (IX) ☆ (X) ○ for NMF+TMU for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of NMF, respectively.

all systems behave as solid phase rotator. Different behavior of polar molecule in different environment seems to be due to azeotropic behavior arising from microscopic inhomogeneity of polar constituents²¹. $\Delta S\tau$'s are -ive for all systems (Table 3). The entropy of a system is a measure of its orderly nature if the environment of the system is cooperative for a particular system. Activated systems are more stable than the normal states, since $\Delta S\tau$'s are -ive. The estimated Debye factor $\tau_{jk}T/\eta$ are almost same order for all the system whereas Kalman factor $\tau_{jk}T/\eta^\gamma$ vary from system to system. This signifies that the systems obey the Debye relaxation mechanism. The chemical structures of the polar molecules are sketched in Fig. 8 from the fixed bond moments²² of substituent polar groups aligned at an angle to the molecular axis. The vectorial addition of bond moments assuming the planer structure of molecules leads to the μ_{theo} as given in Table 3. These also exist differences in electron affinity between two atoms of a substituent polar groups causing intra molecular polarization of adjacent bond by a dipole to yield inductive, mesomeric and electromeric effects in them. The solute-solvent molecular association as evident from Fig. 8(a-c) arises due to interaction of π localized electron cloud of benzene ring and the fractional positive charge δ^+ at the side of C or N-atom of benzotrile, NMF and TMU, respectively. The solute-solute association occurred as a result of interaction of fractional +ive charge δ^+ at the side of C or N-atom of

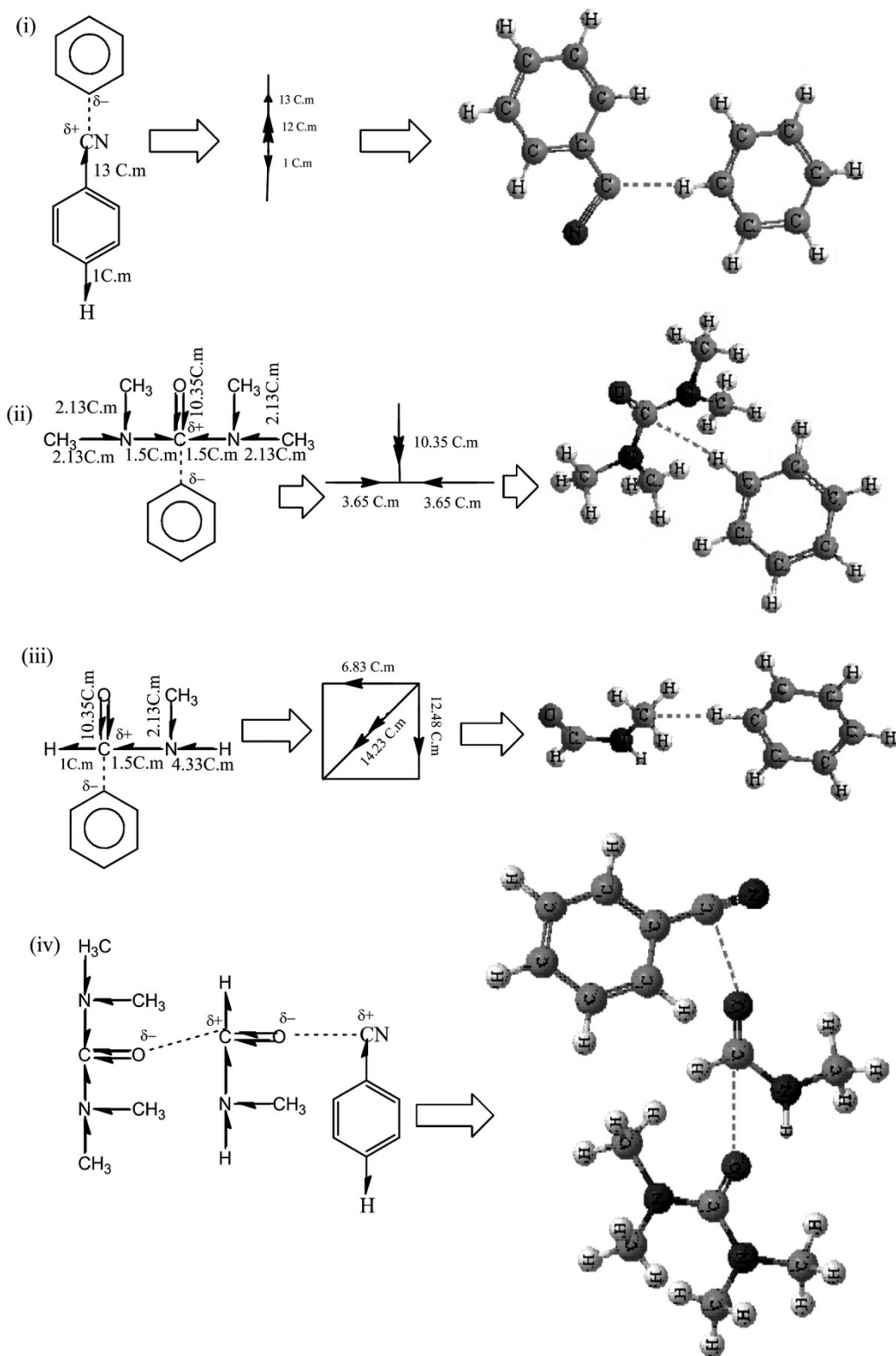


Fig. 8 — Theoretical dipole moment μ_{theo} 's from available bond angle and bond moments (multiples of 10^{-30} C.m) of NMF, TMU and benzonitrile along with solute-solvent and solute-solute molecular associations. (i) benzonitrile - C_6H_6 (ii) TMU - C_6H_6 (iii) NMF - C_6H_6 (iv) TMU- NMF - benzonitrile.

Table 3 — Reports estimated slopes and intercepts of $\ln(\tau_{jk}T)$ against $1/T$ curves, calculated thermodynamic energy parameters like enthalpy of activation ΔH_{τ} in KJ/mole, free energy of activation ΔF_{τ} in KJ/mole, entropy of activation ΔS_{τ} in J/mole.K, Debye factor $\tau_{jk}T/\eta$, Kalman factor $\tau_{jk}T/\eta^{\gamma}$, γ from slopes of $\ln(\tau_{jk}T)$ vs $\ln \eta$ linear equation, $\Delta H_{\eta}=(\Delta H_{\tau}/\gamma)$ in KJ/mole for viscous flow process of binary polar mixture NMF + benzonitrile and NMF + TMU dissolved in C_6H_6 for 0.0, 0.3, 0.5, 0.7 and 1.0 mole fraction of NMF at 25 °C, 30 °C and 25 °C, 30 °C, 35 °C, 40 °C, respectively, under 9.885 GHz electric field.

System	Temperature (°C)	Mole fraction x_j of NMF	Intercepts and slopes of $\ln(\tau_{jk}T)$ vs $(1/T) \times 10^3$		ΔH_{τ} (KJ/mole)	ΔF_{τ} (KJ/mole)	ΔS_{τ} (J/mole.K)	γ from $\ln(\tau_{jk}T)$ vs $\ln \eta$ curve	$\Delta H_{\eta}=(\Delta H_{\tau}/\gamma)$ (KJ/mole)	Debye factor $\tau_{jk}T/\eta$	Kalman factor $\tau_{jk}T/\eta^{\gamma}$
(I) NMF+Benzonitrile in C_6H_6	25	0.0	-19.7938	21	0.174	10.00	-33	0.03494	4.98	4.5345×10^{-7}	3.2532×10^{-9}
	30					10.16	-33			4.8051×10^{-7}	3.2531×10^{-9}
(II) NMF+Benzonitrile in C_6H_6	25	0.3	-18.0505	-510	-4.24	9.84	-47.2	-0.84859	4.9965	4.2613×10^{-7}	3.3286×10^{-11}
	30					10.14	-47.5			4.7621×10^{-7}	3.3286×10^{-11}
(III) NMF+Benzonitrile in C_6H_6	25	0.5	-17.6863	-629	-5.23	9.74	-50.2	-1.04659	4.9972	4.0925×10^{-7}	1.1608×10^{-11}
	30					10.07	-50.5			4.6281×10^{-7}	1.1608×10^{-11}
(IV) NMF+Benzonitrile in C_6H_6	25	0.7	-21.7902	451	3.75	8.67	-16.5	0.75042	4.9972	2.6572×10^{-7}	7.4112×10^{-8}
	30					8.71	-16.4			2.6975×10^{-7}	7.4118×10^{-8}
(V) NMF+Benzonitrile in C_6H_6	25	1.0	-22.4926	671	5.58	8.79	-10.8	1.11647	4.9979	2.7813×10^{-7}	5.0470×10^{-7}
	30					8.77	-10.5			2.7619×10^{-7}	5.0470×10^{-7}
(VI) NMF+TMU in C_6H_6	25	0.0	0.18171	-	-51.02	8.41	-199.4	-7.98595	6.3887	2.3840×10^{-7}	2.5816×10^{-27}
	30			6139.89		7.64	-193.6			17.644×10^{-7}	1.0831×10^{-26}
	35					11.53	-203.1			8.1881×10^{-7}	2.9083×10^{-27}
	40					11.61	-200.1			8.2761×10^{-7}	1.8375×10^{-27}
(VII) NMF+TMU in C_6H_6	25	0.3	1.0394	-	-53.41	7.73	-205.2	-8.30623	6.4301	1.8128×10^{-7}	3.8135×10^{-28}
	30			6426.84		8.20	-203.3			2.2041×10^{-7}	2.6502×10^{-28}
	35					10.98	-209.1			6.6017×10^{-7}	4.3777×10^{-28}
	40					11.45	-207.2			7.8032×10^{-7}	3.1808×10^{-28}
(VIII) NMF+TMU in C_6H_6	25	0.5	-4.82408	-	-38.86	8.09	-157.6	-6.31996	6.1489	2.1008×10^{-7}	1.1443×10^{-23}
	30			4676.62		7.69	-153.6			1.8019×10^{-7}	6.3216×10^{-24}
	35					10.27	-159.5			5.0036×10^{-7}	1.0992×10^{-23}
	40					10.90	-159.0			6.3097×10^{-7}	9.4533×10^{-24}
(IX) NMF+TMU in C_6H_6	25	0.7	-6.07803	-	-36.03	7.71	-146.8	-5.70098	6.32	1.8028×10^{-7}	2.3302×10^{-22}
	30			4335.25		7.65	-144.2			1.7750×10^{-7}	1.5337×10^{-22}
	35					9.90	-149.1			4.3294×10^{-7}	2.4370×10^{-22}
	40					10.29	-148.0			4.9907×10^{-7}	1.9788×10^{-22}
(X) NMF+TMU in C_6H_6	25	1.0	-21.83311	425.23	3.53	8.79	-17.7	0.17183	20.5436	2.7813×10^{-7}	4.0196×10^{-9}
	30					8.77	-17.3			2.7619×10^{-7}	3.7978×10^{-9}
	35					8.52	-16.2			2.5279×10^{-7}	3.2967×10^{-9}
	40					8.86	-17.0			2.8750×10^{-7}	3.5904×10^{-9}

benzonitrile, NMF and TMU with fractional -ive charge δ^- at the side of O atom of $C=O$ group in NMF. The dipole-dipole interaction occurs in such a way that the effective dipole moments get increased. The charge transfer from the fragment of the atoms may also be responsible for the interacting environment arising out of microscopic inhomogeneity of constituent polar groups and azeotropic behavior of the mixture.

5 Conclusions

A simple method is proposed to estimate τ and μ based on Debye model of polar-nonpolar liquid mixture using normalized conductivity data of binary

polar mixture of benzonitrile and TMU with NMF dissolved in C_6H_6 for different w_{jk} 's of solutes and x_j 's of NMF at different experimental temperatures under 9.885 GHz electric field. Solute-solvent (monomer) and solute-solute (dimer) molecular associations are predicted up to $x_j=0.5$ and beyond $x_j=0.5$ to $x_j=1.0$, respectively. The chemical structures μ_{theo} due to inductive, electromeric and mesomeric effects between two adjacent atoms of polar groups arising out of microscopic inhomogeneity and azeotropic behavior in them. Molecular dynamics as well as solvent environment around the polar molecules are ascertained from Eyring's equation. The study reveals that Debye relaxation mechanism holds

goods for binary polar-nonpolar liquid mixture under investigation.

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